

The University of Chicago

A STUDY OF THE REACTIONS OF
PLATINOUS CHLORIDE
DICARBONYL

A DISSERTATION SUBMITTED TO THE
GRADUATE FACULTY IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

By
WALTER OWEN WALKER

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INTRODUCTION

Schutzenberger¹⁻¹⁰ first prepared and studied the compounds formed by the alternate action of dry chlorine and dry carbon monoxide upon platinum sponge heated to approximately 250°. He listed three carbonyls: platinous chloride monocarbonyl (PtCl_2CO), platinous chloride sesquicarbonyl ($2\text{PtCl}_2\text{3CO}$), and platinous chloride dicarbonyl ($\text{PtCl}_2\text{2CO}$). The evidence⁹ adduced by this author for the existence of the sesquicarbonyl is open to a number of objections.

Pullinger¹¹⁻¹⁴ also prepared and studied these compounds and, in addition, proved the existence of a fourth substance, platinous chloride diphosgene ($\text{PtCl}_2(\text{COCl}_2)_2$),

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1. Schutzenberger: Compt. rend., 66, 667 (1868)
 2. Schutzenberger: Ibid., 70, 1134 (1872)
 3. Schutzenberger: Ibid., 70, 1287 (1872)
 4. Schutzenberger: Bull. soc. chim., (2), 10, 188 (1868)
 5. Schutzenberger: Ibid., (2), 14, 24 (1870)
 6. Schutzenberger: Ibid., (2), 14, 97 (1870)
 7. Schutzenberger: Ann. chim. phys., (4), 15, 100 (1868)
 8. Schutzenberger: Ibid., (4), 21, 350 (1870)
 9. Schutzenberger: J. Chem. Soc., 24, 1009 (1871)
 10. Schutzenberger: Ann. Chem. Pharm., 8 suppl., 243 (1872)
 11. Pullinger: Proc. Chem. Soc., 7, 111 (1891)
 12. Pullinger: Trans. Chem. Soc., 59, 598 (1891)
 13. Pullinger: Ber., 24, 2291 (1891)
 14. Pullinger: Chem. Zentr., (4), 3, 453, II (1891)

while Mylius and Foerster¹⁻² and Foerster³ studied the reactions of platinous chloride monocarbonyl with a number of substances. Schutzenberger⁴⁻⁵ had previously investigated the behavior of the monocarbonyl toward ammonia and ethylene, and of the dicarbonyl toward ammonia.

The purpose of this investigation was the preparation of organic derivatives of divalent platinum which were later to be used in studies on complex ion formation. It was discovered early in the work that platinous chloride dicarbonyl reacts unusually slowly with Grignard reagents giving rise to many side reactions in which a large part of the platinum is liberated in metallic or colloidal condition, and that the platinous organic derivatives, for the formation of which some evidence was obtained, are extremely unstable. It was therefore decided that, before further progress could be made in the isolation of the organic platinous compounds, it would be necessary to study qualitatively the behavior of platinous chloride dicarbonyl toward a variety of reagents.

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1. Mylius and Foerster: Ber., 24, 2434 (1891)
 2. Mylius and Foerster: Chem. Zentr., (4), 3, 454, II (1891)
 3. Foerster: Ber., 24, 3751 (1892)
 4. Schutzenberger: Compt. rend., 70, 1287 (1872)
 5. Schutzenberger: J. Chem. Soc., 24, 1009 (1871)

PREPARATION OF PLATINOUS CHLORIDE DICARBONYL.

The first method attempted for the preparation of the dicarbonyl¹ was analogous to that used by Kharasch and Isbell in the preparation of the carbonyl of aurous chloride². A suspension of platinous chloride was treated with carbon monoxide in a liquid in which the dicarbonyl is soluble. While it was possible to obtain small amounts of the dicarbonyl in this way, the method was not satisfactory because of the necessity of using high boiling solvents, from which the final product cannot readily be freed if temperatures high enough for even moderately rapid reaction are employed. Consequently the method of Schutzenberger³ was somewhat modified to yield a purer product than he obtained.

A stream of carefully dried carbon monoxide (generated by the action of formic acid on concentrated sulfuric acid at 80-100°) is passed over platinous chloride at 235-240°. The apparatus is shown in Figure 1. The parts a, b, c, and d constitute the generator for the carbon monoxide and a condenser as a trap for the removal of excess of formic acid; h, i, and j represent the drying train, in which the gas passes in order through sulfuric acid, glass wool,

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1. For brevity, the platinous chloride dicarbonyl will hereafter be referred to as the dicarbonyl.
 2. Kharasch and Isbell: J. Amer. Chem. Soc., 52, 2919 (1930)
 3. Schutzenberger: Loc. cit.

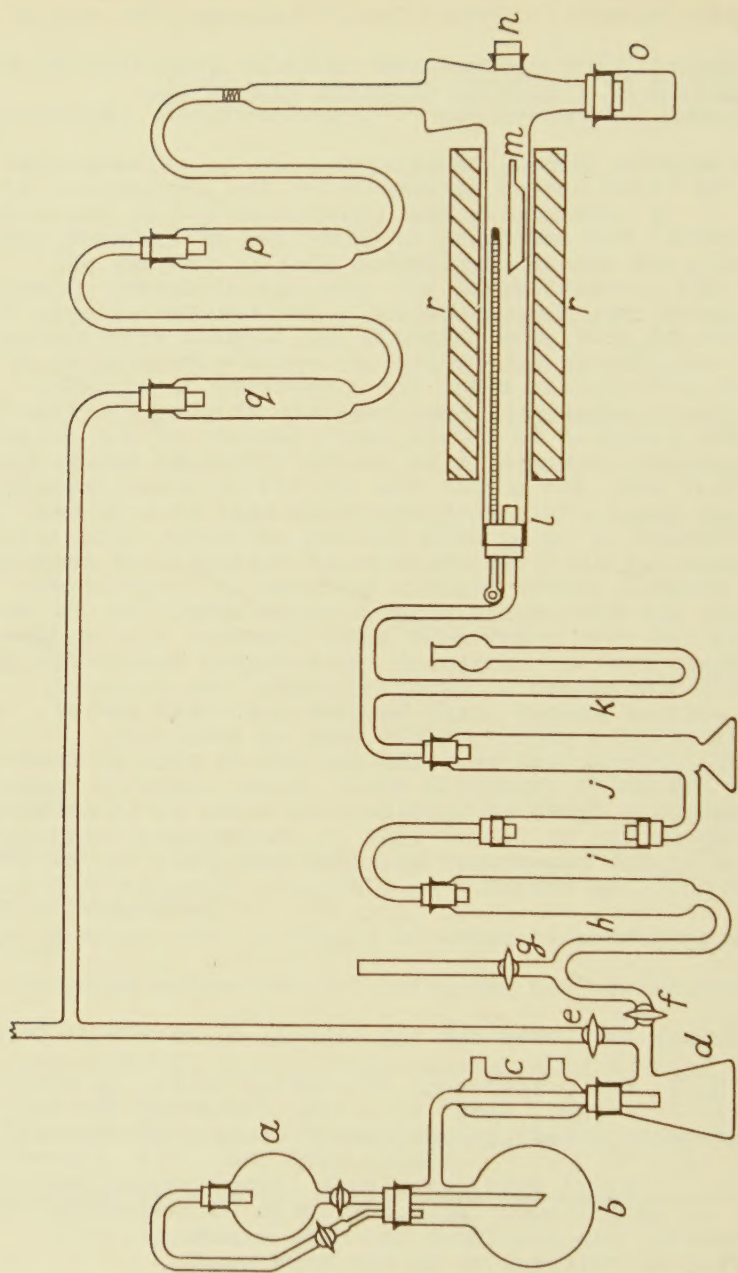


FIG. 1

and phosphorus pentoxide; k is a pressure gauge; l is the reaction tube with a receptacle for collecting the sublimed dicarbonyl; and r is an electric furnace which can be kept constant to within 5° by external resistances. Stopcock e opens the line to a bye pass through which the gas, when the reaction is complete, can be led directly to the hood, and q and p are drying towers which protect the exit tube from moisture. The opening, n, closed by a rubber stopper, is used in rapidly scraping the dicarbonyl from the walls of the receiving vessel and transferring it to the weighing bottle, o, which is attached to the apparatus by a rubber stopper, but which is fitted with a carefully ground stopper to be used when the reaction product is stored.

Before carbon monoxide is passed over the platinous chloride contained in the porcelain boat, m, dry air is passed through the apparatus at $230-240^{\circ}$. Carbon monoxide is then admitted and passed through the vessel just rapidly enough to carry the vapors of the dicarbonyl into the receiver, but not fast enough to carry the crystals into p. A small plug of glass wool in the tube leading to p helps retain the finer crystals of the dicarbonyl. While the dicarbonyl is removed to the weighing bottle, o, the stream of carbon monoxide is allowed to flow to prevent diffusion of moisture into the apparatus through n.

Of particular importance is the position of the boat. If it is introduced too far into the tube, the dicarbonyl is partly decomposed during its passage to the re-

ceiver. The failure of earlier investigators to obtain a white product is due to their use of a long tube filled with platinum sponge and heated throughout its length, for the dicarbonyl, formed in the presence of an excess of carbon monoxide near the inlet portion of the tube, is partially decomposed before it sublimes out of the other end. While the procedure used by us is slow, it produces a pure product. Attempts to hasten the reaction; e. g., by mixing the platinum with silica gel to secure a larger reaction surface, were unsuccessful because under these conditions it seemed impossible to maintain, throughout the tube, a high enough concentration of carbon monoxide to prevent decomposition of the dicarbonyl.

This procedure always left a slate-colored residue of undetermined composition in the boat, but yielded a dicarbonyl of a fairly high degree of purity as evinced by its color, its composition, and the sharpness of its melting point. For example, the average platinum content in two samples was 59.63%, theory 60.6%, while the average chlorine content in three samples was 21.65%, theory for PtCl_2CO 22.02%. These results may be considered very satisfactory in view of the instability of the dicarbonyl and of its reactivity toward moisture. Thus, although the dicarbonyl prepared as described is usually nearly pure white, the slightest trace of moisture produces a yellow product; even an atmosphere containing only a very small amount of moisture induces the color change in half an hour and longer exposure

finally causes the product to become black. On moist days, it is impossible to transfer the material from vessel to vessel; in dry weather, the product can be handled without undue difficulty if exposure to ordinary air is made as short as possible. The instability of the dicarbonyl is shown by the fact that its melting point must be determined in an atmosphere of carbon monoxide, under which condition it melts at 142° ; if it is heated in dry air, the melting point first falls to 125.3° , and then rises to approximately 185° . This phenomenon is usually attributed to decomposition of the dicarbonyl to form the sesquicarbonyl $2\text{PtCl}_2\text{CO}$, and then the monocarbonyl PtCl_2CO . As a matter of fact, color and melting point are better criteria of purity than the analysis. Thus a mixture of equal parts of the dicarbonyl and the sesquicarbonyl has a platinum content of 61.89%, while the pure dicarbonyl contains 59.63% of platinum. Small amounts of the sesquicarbonyl would therefore affect the analysis very little¹.

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1. For analysis, a known weight of the dicarbonyl was decomposed by the addition of 25 c.c. of water and 1 c.c. of concentrated ammonia. When the reaction is complete, the mixture is heated to boiling and the solution filtered from the precipitated platinum. The latter is weighed in the usual way and chlorine determined in the filtrate. (See Mylius and Foerster: Ber., 24, 2424 (1891).)

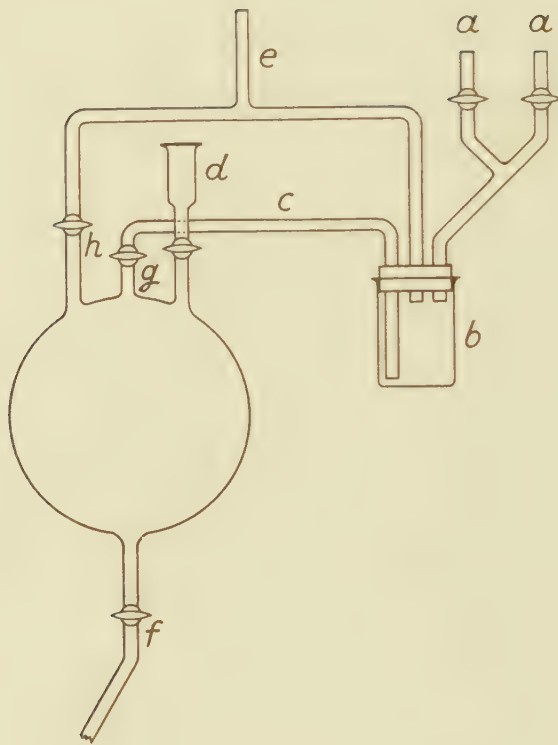


FIG. 2

REACTIONS OF PLATINOUS CHLORIDE DICARBONYL WITH GRIGNARD
REAGENTS.

The reactions of the dicarbonyl and Grignard reagents were carried out in a 500 c.c. apparatus of the usual type which was equipped with a motor stirrer, reflux condenser, an opening for sampling the contents of the flask and another opening into which the tube f of the apparatus shown in Figure 2 was inserted. This second apparatus was necessary because of the sensitiveness of the dicarbonyl to moisture. The procedure of mixing the reagents was as follows: Tube a is connected to a reservoir for dry benzene, a small portion of which can be forced by dry air into the receptacle b containing a weighed portion of the dicarbonyl. By applying a pressure of dry air to e, the mixture can be agitated and the process of solution hastened. When the benzene seems saturated with dicarbonyl, stopcock g is opened and the clear liquid is forced into the bulb. Additional benzene is introduced into b and the process repeated until all of the dicarbonyl is dissolved and transferred to the bulb. The whole amount is then allowed to run through f into the Grignard apparatus proper. The Grignard reagent, prepared and carefully filtered out of contact with moisture, is then introduced through tube d, after which it is diluted to a volume of 75 c.c. with ether, brought in through tube a. Tube e, protected from moisture, is used to equalize the pressures in the apparatus.

The first of the series of Grignard reactions was that between the dicarbonyl and phenyl magnesium bromide. The procedures and results are described in some detail because they influenced the direction of subsequent experiments. A solution containing approximately one g. of the dicarbonyl in 50 c.c. of benzene was diluted with dry ether, in the reaction vessel just described, to a total volume of about 175 c.c. and the mixture cooled to 0°. The Grignard reagent, diluted to about 100 c.c. with ether, was then allowed to flow dropwise into the dicarbonyl solution during a period of an hour with constant stirring and cooling as is customary in such reactions. In most of the experiments, the molar ratio of Grignard reagent to dicarbonyl was 5:1. Usually during this time some platinum was formed. In the most favorable experiments, the resulting solution was straw colored; in less favorable cases, the mixture turned black or precipitated red or greenish colloidal coagulums; while in the most unfavorable cases a sticky mass, probably a mixture of platinum and magnesium hydroxide was obtained. Slow addition of the Grignard to the dicarbonyl gave the most favorable results; changes of concentration were without effect, and reversal of the order of addition was decidedly disadvantageous.

After all of the Grignard reagent had been added, the mixture was allowed to come slowly to room temperature, and was then filtered and poured upon crushed ice suspended in 2% sulfuric acid to decompose unchanged dicarbonyl and Grignard

reagent. At this stage of the procedure, there always occurred some precipitation of platinum, most of which collected in the water layer of the mixture. The two layers were separated, the aqueous solution was repeatedly extracted with ether and all of the ethereal extracts were combined, washed with water, and dried with sodium sulfate or calcium chloride. This procedure removed any suspended platinum by adsorption. Evaporation of the ether left a dark brown syrupy material from which crystals of diphenyl were isolated. Repeated efforts to identify other compounds were unsuccessful. The platinum content (approximately 22%) of the syrupy material decreased on standing, due to precipitation of the metal.

The foregoing procedure was modified in several ways, none of which led to identification of the other constituents of the reaction products. These modifications were: (a) changing the reaction temperature from -15° to room temperature; (b) decomposing the excess dicarbonyl and Grignard reagent with water, acetic acid, alcohol, ligroin, or hydrochloric acid; (c) eliminating the decomposition of the excess dicarbonyl and Grignard by 2% sulfuric acid solution and, in its stead, removing the solvent in vacuo followed by extraction of the residue with ether; (d) washing the ethereal extracts with dilute sodium bicarbonate solution and varying the time and temperature of drying; (e) shaking an ethereal solution of the syrup-like substance with silver cyanide in an effort to obtain a more readily crystallizable platinum derivative; and (f) carrying out the entire procedure

in a dark room.

In spite of these negative results, the quantity of diphenyl obtained gives indirect evidence for the formation of an organic platinum compound. In the reaction, approximately 0.48 g. of diphenyl is formed per g. of dicarbonyl. On the other hand, from an equivalent amount of the Grignard reagent alone, diluted with benzene and ether, but without addition of the dicarbonyl, only 0.12 g. of diphenyl was formed in a corresponding interval of time as a result of spontaneous decomposition of the reagent. The excess, 0.36 g., obtained when the dicarbonyl was added, must therefore be due to the decomposition of an unstable, intermediate organic platinum compound. The maximum amount of diphenyl obtainable in this way is 0.475 g.; in view of the fact that the reaction between the dicarbonyl and the Grignard reagent undoubtedly did not go to completion¹, the yield of diphenyl is fairly conclusive evidence of the formation of the above-mentioned

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1. To determine the rate of reaction, Grignard reagent and dicarbonyl were mixed in equimolecular proportions and the mixture allowed to stand for 15 minutes. A sample of the mixture gave a copious precipitate of platinum when treated with water, thus indicating the presence of a large amount of unchanged dicarbonyl. An additional 0.2 mol of Grignard reagent was added and another test made. Not until the ratio of Grignard reagent to dicarbonyl became about 3:1 and approximately 15 hours had elapsed was there a marked diminution in the amount of platinum precipitate. This shows the reaction to be extremely slow. Nevertheless, in the experiments described above, the total time of interaction was limited to about two hours to avoid undue loss of platinum by spontaneous decomposition.

compound. These results suggested changing the nature of the Grignard reagent with the objective of obtaining a more stable compound.

Benzyl magnesium chloride was allowed to react with the dicarbonyl under conditions similar to those employed with phenyl magnesium bromide. The products of this reaction were dibenzyl and a brown syrup possessing properties similar to those of the material obtained in the preceding experiment. The yield of dibenzyl was approximately 0.28 g. per g. of dicarbonyl, whereas approximately 0.14 g. of dibenzyl was obtained from the blank Grignard reagent as described above. Obviously the yield of dibenzyl is relatively smaller than that of diphenyl in the corresponding reaction already described; this probably indicates that benzyl magnesium chloride reacts much less completely than does the phenyl derivative.

The results with alpha-naphthyl magnesium bromide were still less successful. Instead of dinaphthyl, the typical brown syrup contained large amounts of naphthalene due, obviously, to interaction of the unchanged Grignard reagent with water.

The use of ethyl magnesium bromide, on the other hand, led to much more favorable results, although even in this case no pure platinum compound was isolated. But the ethereal layer of the mixture resulting from treatment of the reaction product with ice and 2% sulfuric acid yielded a small quantity of white, needle-like crystals. They melt-

ed at 49-51°; were soluble in benzene, in ether, and in ligroin, but could not be purified by crystallization from these solvents because the excess of solvent could not readily be removed. Their average platinum content was over 50% - an amount too large to be accounted for by the assumption of adsorbed colloidal platinum, but nevertheless not large enough for any platinum compound likely to result from the reaction. That they represent an impure sample of an organic platinum compound is shown by the fact that they readily turn black by liberation of platinum on exposure to moist air. The ethyl derivatives are evidently more stable than the phenyl and benzyl derivatives and should be obtainable when large quantities of dicarbonyl are available for their preparation.

Inasmuch as the failure to obtain the desired platinum compounds was undoubtedly due not only to their instability under the conditions of our experiments, but largely to the slowness of the reactions between the dicarbonyl and the Grignard reagents, an attempt was made to substitute the more active zinc diethyl for the latter. But the reaction led to rapid reduction of the dicarbonyl to metallic platinum. No other products were isolated.

The foregoing results indicate that, by suitable choice of reagents and procedures, organic derivatives of platinum should be obtainable from the dicarbonyl as starting material. But before such a result can be achieved, it will be necessary to study the behavior of the dicarbonyl

toward various reagents in order to choose the best conditions for the reaction. Most important among these reagents are reducing agents and compounds likely to react by addition. The following preliminary qualitative studies are to be supplemented by quantitative experiments to be undertaken later.

THE BEHAVIOR OF PLATINOUS CHLORIDE DICARBONYL TOWARD REDUCING AGENTS.

Reactions with Alcohols:

Fairly concentrated solutions of the dicarbonyl in benzene were treated separately with thoroughly dried samples of methyl and ethyl alcohol and with primary, secondary, and tertiary butyl alcohols. In each case, platinum was liberated as a slightly colored colloidal suspension which gradually turned darker and finally precipitated out as finely divided metal.

In order to make sure that these results were not due to traces of water which could have caused the precipitation of platinum, the solution of the dicarbonyl was added to the alcohol in two portions. The first portion removes the moisture by interacting with it; any reaction observed on addition of the second portion of the dicarbonyl must be due to reaction of the dicarbonyl with the alcohol itself. In every case, the second portion behaved just as did the first. Further confirmation of this conclusion is found in the fact that the alcohol is in every case oxidized as was demonstrated

by distilling the residual liquid, after the reaction had gone to completion, and proving the presence of an aldehyde in the distillate by means of Schiff's reagent.

Although the reaction of methyl alcohol with the dicarbonyl was moderately slow, requiring approximately a day for completion, it was much more rapid than that of the ethyl or primary butyl alcohol; the latter reacted most slowly, for even after three days a very considerable amount of unchanged dicarbonyl could be detected by the addition of water. Secondary butyl alcohol reacted somewhat more rapidly than the primary and the tertiary liberated platinum quite rapidly. The latter reaction may, however, have been due to an elimination of water from the alcohol with the formation of isobutylene, rather than the reduction of the dicarbonyl by the alcohol itself.

Benzyl alcohol reacted fairly rapidly with the dicarbonyl, yielding benzaldehyde and platinum; resorcinol and hydroquinone behaved in analogous fashion.

Reactions with Acids:

Formic acid (Sp. Gr. 1.2), glacial acetic acid, dried by means of acetic anhydride or of phosphorus pentoxide, acetic anhydride, freshly distilled butyric acid, and valeric acid liberated platinum from the dicarbonyl. Even in the case of formic acid, the reduction of the dicarbonyl was slow, failing to reach completion in an hour although a large excess of the acid was used; the other acids reacted still

more slowly. In the case of butyric acid, the reaction was still incomplete after a period of three days, and with valeric acid a much longer time seemed to be required. The changes were not further investigated¹.

Action of Bromine on the Dicarbonyl.

The dicarbonyl reacted with bromine extraordinarily slowly. Thoroughly dried and carefully distilled bromine was added to about 0.1 g. of the substance. After an hour, the excess of bromine was removed in vacuo and the reddish crystalline residue dissolved in water. The resulting precipitation of platinum indicated that some unchanged dicarbonyl remained; the major portion of the platinum had been oxidized to the platinic state as indicated by the formation of potassium iodo platinate with potassium iodide. In another reaction twelve hours of contact between the bromine and dicarbonyl led to the formation of a crystalline mass containing 47.88% of platinum. This shows that nearly all of the platinum had been oxidized, for the compound PtCl_2Br_2 or an equimolecular mixture of platinic chloride and bromide has a platinum content of 45.85%. Longer treatment with excess of bromine at room temperature led to the formation of an impure product which apparently consisted largely of platinic bromide, since it had a platinum content of 36.84%,

1. Salicylic and benzoic acids do not seem to react with the dicarbonyl.

as compared with 37.91% platinum calculation for PtBr_4 . When the reaction was carried out in a sealed tube at 90-100° over a period of five days, a purer sample of the tetrabromide (% Pt: 37.54) was obtained.

Unexpected and as yet unexplained results were obtained when small quantities of the dicarbonyl were treated with bromine in carefully dried carbon tetrachloride¹. A solution containing 0.05 g. of the dicarbonyl and an excess of bromine was boiled vigorously until the reaction appeared to be complete as judged by the failure of the solution to give a precipitate of platinum when treated with water. The carbon tetrachloride and the excess of bromine were then removed by evaporation and the residue was dissolved in water. The resulting solution did not give the characteristic iodide test for tetravalent platinum. Obviously the carbon tetrachloride solution of bromine decomposed the dicarbonyl without oxidation of the platinum; yet the product was not platinous chloride or bromide because it is soluble in water. The aqueous solution of the reaction product is very readily oxidized to the platinic condition by bromine water.

In these experiments the quantity of dicarbonyl was so small that there was no possibility of studying further the nature of the reaction products. Efforts to obtain quan-

1. Bromoform, carbon disulfide and benzene were also used. The disulfide and bromoform solutions behaved just as did the carbon tetrachloride solution, whereas bromine acted on benzene more readily than on the dicarbonyl.

titles large enough for analysis failed because, when the amount of the dicarbonyl was increased, spontaneous decomposition set in long before reaction with the bromine was complete. Nor was it possible to hasten the reaction by the use of higher temperatures for, under these conditions, platinic compounds, instead of the unknown platinous derivative, were obtained. Thus, when a carbon tetrachloride solution of bromine was refluxed for thirty hours with 0.5 g. of the dicarbonyl, a precipitate was formed having the composition, PtCl_2Br_2 , as shown by its platinum content (44.74%, calculation for PtCl_2Br_2 , 45.85%). The low platinum content is probably due to the formation of some platinic bromide. Further investigation of the reaction is necessary before any definite conclusions are reached.

Iodine dissolved in carbon tetrachloride does not react with solutions of the dicarbonyl in carbon tetrachloride, carbon disulfide, bromoform, or benzene.

BEHAVIOR OF THE PLATINOUS CHLORIDE DICARBONYL TOWARD REAGENTS
WITH WHICH IT MAY ACT BY ADDITION.

Acetamide:

A saturated solution of acetamide in a mixture of benzene and carbon tetrachloride, containing 50% of each solvent by weight, was added to a solution of 2 g. of the dicarbonyl in approximately 100 c.c. of benzene. A yellowish suspension appeared immediately, but turned black in the course of an hour after which a precipitate of platinum formed

slowly. The mixture was allowed to stand for four or five days, during which time greenish-yellow crystals formed on the sides and bottom of the flask. The liquid was decanted, the crystals washed with benzene and recrystallized from ether. They melted at $87-91^{\circ}$ and decomposed at a higher temperature. The substance was soluble in ethyl alcohol, in acetone, and in water. In the last-named solvent, decomposition and separation of platinum took place rapidly. Decomposition also occurred in moist air. The crystals were insoluble in ligroin, in carbon tetrachloride and in benzene. Three samples of approximately 0.125 g. each had an average platinum content varying from 41.47-42.61% and gave a positive test for chlorine. The average value of 43.04% agrees best with the platinum content (41.42%) of a compound having the formula $\text{PtCl}_2\text{CO}(\text{CH}_3\text{CONH}_2)_3$.

Diethyl Sulfide:

When diethyl sulfide was added to a solution of the dicarbonyl in benzene, the mixture effervesced strongly, liberating carbon monoxide. The resulting clear, yellow liquid was allowed to stand for an hour in order to complete the reaction. Bright yellow crystals and some amorphous yellow material was formed when the solvent was removed in vacuo. A finely ground sample of this mixture softened at 90° and melted at $98-99^{\circ}$. It began to decompose at 220° , leaving an amber colored residue in the melting tube. The yellow crystals were quite soluble in ether, in benzene, in

ethyl alcohol, and in carbon tetrachloride; slightly soluble in water and in cold ligroin; but very soluble in hot ligroin, from which they precipitated completely on cooling to 0°.

Attempts were made to purify the mixture by crystallization from various solvents. The best results were obtained with ligroin. The material was divided into two fractions by cooling a ligroin solution, saturated at the boiling point, to 30°, removing the crystals so formed, and cooling the residual solution to 0° to obtain a second fraction. By this procedure, the melting point range of the material was raised from 98-99° to 99-102° for the second fraction and to 104-105° for the first fraction. But the platinum content was not greatly changed by this treatment. The original sample had an average platinum content of 42.62%; the fraction crystallized at 0°, 42.43%; and that crystallized at 30°, 42.18%. All of these analytical results are in fair agreement with the platinum content (43.72%) of the compound $\text{PtCl}_2(\text{Et}_2\text{S})_2$ obtained by Angell, Drew, and Wardlaw¹. Obviously our sample was not entirely pure.

Pyridine²:

The dicarbonyl dissolves readily in pyridine form-

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1. Angell, Drew, and Wardlaw: J. Chem. Soc., 349-69 (1930)
 2. The addition of 2 c.c. of methyl isocyanide to 10 c.c. of a highly concentrated solution of the dicarbonyl in benzene resulted in the formation of a curdy, yellowish white precipitate and a gas. The precipitate, which crumbled to a white powder on drying, was insoluble in benzene and in ether, but readily soluble in alcohol. The platinum content (35.34%) of this precipitate indicated that it was quite impure. The solid was not further investigated.

ing a dark green solution. After several hours, platinum precipitated from this solution, together with a very small quantity of colorless crystals, the identity of which could not be established, because of the small amount of material available.

Hexamethylene Tetramine:

A white precipitate was formed when a saturated solution of hexamethylene tetramine in carbon tetrachloride was added to a concentrated benzene solution of the dicarbonyl. The mixture was allowed to stand until precipitation was complete, after which the solid material was collected on a sintered glass filter, washed three times with dry benzene, and then allowed to dry in air. It was soluble, with slight decomposition, in water, in alcohol, and in glacial acetic acid. It was insoluble in benzene, in ether, in ligroin, and in carbon tetrachloride. It decomposed, without melting, at 150-190°. The material gave qualitative tests for platinum, carbon, and chlorine. Analysis of an air dried sample gave a platinum content of 34.93%; while another sample, dried at 90° for ten hours, gave 35.44%. While these analyses agree closely with the platinum content (35.70%) of a compound $\text{PtCl}_2((\text{CH}_2)_6\text{N}_4)_2$, the results could not be duplicated. Other preparations similarly prepared and similar in appearance varied in platinum content from 38.3% to 40.15%, while in several instances black products of low platinum content were obtained. Since no solvent could be found in which de-

composition of the substance did not occur, crystallization was impossible.

REACTIONS OF PLATINOUS CHLORIDE DICARBONYL WITH UNSATURATED COMPOUNDS.

Approximately 0.2 g. of the dicarbonyl was dissolved in 25 c.c. of dry amylene. The reaction evolved enough heat to boil off considerable quantities of amylene, but no carbon monoxide was given off as shown by analysis of the evolved vapor. To complete the reaction, however, heat had to be applied. A deposit, presumably platinum, was formed in the reaction flask. A brown, resinous substance, containing platinum, carbon, and chlorine, remained when the solution, after filtering, was evaporated to dryness in vacuo. It was soluble in amylene, in ligroin, in ether, in benzene, in carbon tetrachloride, in acetone, and in ethyl alcohol, but could not be crystallized from any of these solvents.

This substance gave an average platinum content of 38.88% when it was dried in vacuo at 60°¹. At room temperature, it was impossible to remove completely the excess of amylene, while at temperatures much above 60°, decomposition occurred. This platinum content corresponds to a compound having the formula $\text{PtCl}_2\text{CO}(\text{C}_5\text{H}_{10})_3$ (theory 38.67%). However,

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1. For this purpose, the apparatus shown in Figure 3 was employed. It consists of a vacuum desiccator surrounded by a vapor jacket, the lower part of which acts as a reservoir for the boiling liquid.

the analysis alone is insufficient evidence for the identification of the substance.

Both oleic acid and styrene appeared to react very slowly with the dicarbonyl, although no products were isolated from either reaction mixture.

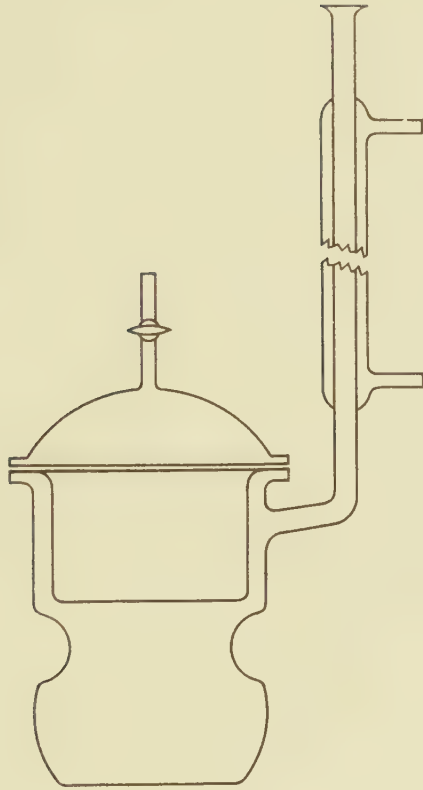


FIG. 3

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The writer wishes to acknowledge his indebtedness to Professors H. I. Schlesinger and M. S. Kharasch, at whose suggestion and under whose direction this work was carried out.

